NS-11-1-K-W

STM-Controlled single-molecule optical spectroscopy

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Control of optical properties of single molecules by plasmonic nanostructures is an important issue in nanoplasmonics and nanophotonics, particularly valuable for the development of molecular plasmonic devices and ultrasensitive high-resolution microscopic techniques. The nanocavity defined by the metallic tip and substrate in a scanning tunneling microscope (STM) can provide highly localized and dramatically enhanced electrical fields upon appropriate plasmonic resonant tuning, which can modify the excitation and emission of a single molecule inside and produce interesting new optoelectronic phenomena [1]. In this talk, I shall demonstrate two STM-induced phenomena related to single-molecule optical spectroscopy. The first is single-molecule Raman scattering. The spatial resolution of tip enhanced Raman spectromicroscopy has been driven down to sub-nanometer scale for a single porphyrin molecule [2]. I shall also demonstrate the chemical distinguishing of adjacent different molecules on a surface [3], one of the ultimate goals for nanoscale identification in nanotechnology. These advances may provide new opportunities for areas related to surface science, catalysis, photochemistry, and even bio-molecular imaging. The second phenomenon is single-molecule electroluminescence. I shall first present well-defined molecule-specific electroluminescence arising from the intramolecular HOMO-LUMO transitions of an isolated single molecule. Then, by using STM manipulation to construct a molecular dimer, I shall demonstrate the visualization of coherent intermolecular dipole-dipole coupling in real space through sub-nanometer resolved electroluminescence imaging [4]. The spatial distribution of the excitonic coupling for different energy states in a dimer indicate that the behavior of the coherent dipole-dipole coupling well resembles the σ and π orbitals in a molecule, revealing the local optical responses and their correlations with transition dipole orientations and phase relations. Furthermore, enhanced electrically driven 'single-molecule' superradiance can be generated by site-selective excitations in constructed oligomers. These findings provide unprecedented spatial details about the coherent dipole-dipole coupling in molecular systems, which may open up new research avenues to study molecular interactions and enable rational engineering of light harvesting structures and quantum light sources.

References

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